CHAPTER 1

INTRODUCTION

1.1 Research Background

Csicsery (1995) had outlined several challenges that the chemical industry will face during the next decades. One of them is diminishing of raw material supplies and therefore, the increasing need to use other available sources such as natural gas, syngas and biomass.

In 1899, Rudolf Diesel tested vegetable oil as fuel for his diesel engine (Shay, 1993). In the 1930's and 1940's vegetable oils were used as diesel fuels but only in emergency situations (Ma and Hanna, 1999). Since the oil embargo in the 70's, newfound interests in alternative energy have seen more research being done on this subject. Due to climate constraints, most of the researches were limited to vegetable oil that are home grown, such as sunflower oil in Turkey (Yorgun *et al.*, 2001), tiger nut oil in Nigeria (Barminas *et al.*, 2001) and canola oil in Canada (Prasad and Bakhshi, 1985; Prasad *et al.*, 1986a,b; Adjaye and Bakhshi, 1995a,b,c; Katikaneni *et al.*, 1995; Idem *et al.*, 1997).

Malaysia is the largest producer of palm oil (Ibrahim and Ahmad, 1993), thus it is imperative for us to exploit this abundant resource. The production of crude palm oil (CPO) in the 2004 is 28.7 million tones and this figure is expected to rise steadily (Foreign Agricultural Service, 2004). Tables 1.1 and 1.2 below show that Malaysia has consistently been the largest producer and exporter of CPO in the world.

Table 1.1: World major producers of palm oil–Tonnes (Foreign Agricultural Service, 2004)

	2000/2001	**2001/2002**	**2002/2003**	**2003/2004**	**2004/2005 (f)**
Malaysia	11,937	11,858	13,180	13,416	14,000
Indonesia	8,300	9,200	9,800	10,600	11,500
Nigeria	730	760	770	780	800
Thailand	580	780	640	840	780
Colombia	560	518	540	575	605
Papua New Guinea	330	370	380	380	380
Ecuador	245	300	320	340	340
Cote d'Ivoire	248	260	234	310	310
Others	1,353	1,373	1,398	1,445	1,447
TOTAL	**21, 821**	**25,419**	**27,262**	**28,686**	**30,162**

Note:
(f)forecast

Table 1.2: World major exporters of palm oil–Tonnes (Foreign Agricultural Service, 2004)

	2000/2001	**2001/2002**	**2002/2003**	**2003/2004**	**2004/2005(f)**
Malaysia	10,475	10,500	11,650	11,765	12,200
Indonesia	4,776	5,979	6,600	7,000	7,650
Papua New Guinea	320	328	326	367	315
Singapore	177	177	212	208	210
Colombia	69	91	108	150	160
EU-25	199	136	149	149	150
Others	686	616	767	886	850
TOTAL	**16,702**	**17,827**	**19,812**	**20,525**	**21,535**

Note:
(f)forecast

Most of the researches done on palm oil conversion are using refined, bleached, deodorized (RBD) palm oil. This is due to the high viscosity of CPO, which cause problems such as incomplete combustion, poor fuel atomization and coking of fuel injectors if used directly without treatment (De Filippis *et al.*, 1995).

Catalytic conversion of palm oil to fuels been performed using various catalysts, most notably ZSM-5 (Ani and Salam, 1995; Tan *et al.*, 1997,1999; Twaiq *et al.*, 1999; Amin and Kasim, 2001a,b). The use of ZSM-5 catalyst is due to the fact that it favors the conversion of n-alkanes to aromatics and this zeolite selectively cracks low octane components into higher-octane components (Nalbandian *et al.*, 1994; Adjaye and Bakhshi, 1995b).

Acidity and shape selectivity of catalysts are governed by several factors such as acidity, pore size and its distribution and also shape of the pores (Twaiq *et al.*, 1999; Adjaye and Bakhshi, 1995a). Beta and Y are both large pore zeolites and acidic in nature. Corma *et al.* (1988) studied the activity and selectivity for zeolite Beta and compared it with zeolite Y. They found that H-Beta is more active in n-heptane cracking than H-Y, while for gas oil cracking the opposite occurs. Hybrid catalysts were used to increase the shape selectivity of catalyst (Twaiq *et al.*, 1999).

The use of zeolite in catalytic cracking has been under study and several have been commercialized. The re-discovery of the MCM-41 materials in 1992 (Kresge *et al.*, 1992) has spurred a lot of interest from researchers in catalysis because there is a need for zeolite-like materials with bigger pore sizes to process heavier hydrocarbons efficiently. This material has been synthesized using different methods such as hydrothermal, sol-gel, grafting and template cation exchange method (Kugita *et al.*, 2003). The difference in synthesis methods resulted in different acidity and thus, different activity of catalyst.

1.2 Problem Statement

Vegetable oil as liquid fuels has long been the subject of interest among researchers. The oil crisis in the mid-80's only served to enhance the work to explore various possibilities to convert vegetable oil to liquid fuels. Vegetable oil has a high viscosity and this would lead to a number of problems in engines.

The introduction of shape selective catalyst (Weisz *et al.*, 1979) in vegetable oil cracking was an important one because this opened up a new horizon in catalysis by zeolites. Since then, vegetable oil cracking was performed by molecular sieves and the results were encouraging (Prasad and Bakhshi, 1985; Prasad *et al.*, 1986a,b; Adjaye and Bakhshi, 1995a,b,c; Ani and Salam, 1995; Twaiq *et al.*, 1999). ZSM-5 was often used, either as single catalyst or hybrid with other zeolites. However, the use of microporous zeolite limits their uses to small molecules. Thus, the discovery of mesoporous materials known as MCM-41 (Beck *et al.*, 1992) was crucial in catalysis. This material provided the mesoporosity needed for cracking larger molecules, though its weak acidity was a major challenge for its use in acid catalysis (Hunger *et al.*, 1999).

Catalytic cracking of palm oil to gasoline has been performed for over a decade. It was shown that palm oil could be converted to gasoline using shape selective catalysts, as reported by several researchers (Ani and Salam, 1995; Salam, *et al.*, 1997; Tan *et al.*, 1997, 1999; Twaiq *et al.*, 1999; Amin and Ekramul, 1999; Amin and Kasim, 2001a, b; Kasim, 2001). Nevertheless, liquid products formed from these catalysts were enriched in aromatics, which need to be eliminated in order to obtain "clean" fuel. Thus, the addition of hydrogen might serve to increase hydrogenation activity, while decreasing coke formation (Shishido and Hattori, 1996a). The challenges lie in the effective usage of hydrogen, whether prior to cracking or during cracking as a diluent.

1.3 Research Questions

Based on the problem statement in the previous section, two questions emerged:

1. Can the microporous-mesoporous materials used in this study achieve high conversion without sacrificing the selectivity towards gasoline?
2. Will hydrocracking and hydrotreatment be significant in improving the gasoline product distribution towards minimizing aromatics production?

1.4 Objectives of Study

The objectives of this research are:

1. To investigate the catalytic activity of MCM-41/ZSM-5 composite catalysts.
2. To analyze the effect of hydrocracking and catalyst hydrotreatment towards catalytic performance of the MCM-41/ZSM-5 composite catalysts.

1.5 Scopes of Study

Generally, this research is divided into 3 phases. In phase 1, composite catalysts of MCM-41/ZSM-5 are synthesized using two different methods. Catalyst characterizations are done in order to know the physicochemical properties of this catalyst.

In the second phase, preliminary observation on the composite catalysts prepared by the different methods is performed in order to choose the catalyst for the next phase of catalytic testing. Thereafter, the chosen composite catalyst from the previous stage is tested for palm oil cracking at different temperatures to study its catalytic performance.

The next phase is testing the composite catalyst with the addition of hydrogen. The first part involved hydrogen addition during cracking (hydrocracking). The effects of temperature and hydrogen to palm oil molar ratio towards hydrocracking are tested. The second part consists of hydrogen addition prior to cracking (catalyst hydrotreatment). The effect of catalyst hydrotreatment is studied at different hydrotreatment flow rates and duration.

1.6 Layout of the Thesis

This thesis reports the research conducted on the effect of hydrogen on palm oil cracking over MCM-41/ZSM-5 composite catalysts. The thesis is divided into six chapters, starting with literature study from past works, followed by results from present work and recommendations for future works.

Chapter 1 imparts the introduction, problem statement, research questions, objectives and scopes of research. This chapter is brief and serves to present the overview of the work conducted in this research.

Chapter 2 reviews previous works related to this study. The physical and chemical properties of palm oil are presented, as well as the properties of catalysts used. Past works on vegetable oil cracking, especially on palm oil conversion to liquid fuels are described in detail. This chapter also looks into the synthesis of

composite catalysts and factors affecting final product from different synthesis conditions.

Chapter 3 reveals the research design and methodology employed in this work. This chapter describes all raw materials used and the experimental rig set up. The synthesis and experimental procedure are also explained in depth in this chapter. Moreover, the research design and independent variables are clarified in the end of this chapter.

Chapter 4 discusses the effect of temperature on palm oil cracking over MCM-41/ZSM-5 composite catalysts. The first part of this chapter deals with the results from catalyst characterizations. Thereafter, this chapter discusses the preliminary selection of composite catalysts prepared by different methods and also looks into the effect of Si/Al ratio on palm oil cracking. Finally, temperature effects on palm oil cracking over the selected composite catalyst are discussed.

Chapter 5 analyses the effect of hydrogen on palm oil cracking over composite catalyst. The hydrogen effects are discussed from two different angles: hydrogen addition during cracking (hydrocracking) and hydrogen addition prior to cracking (catalyst hydrotreatment).

Finally, Chapter 6 gives the general conclusions derived from this study and also suggests some recommendations for future works.